Short communication

Development of gas chromatographic methods for the analyses of organic carbonate-based electrolytes

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HIGHLIGHTS

- Investigations on the stability of organic carbonate-based electrolyte systems.
- Headspace (HS) sampling for the investigation of electrodes.
- Identification of decomposition products with a new method in commercially available electrolytes and self-assembled cells.

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ABSTRACT

In this work, novel methods based on gas chromatography (GC) for the investigation of common organic carbonate-based electrolyte systems are presented, which are used in lithium ion batteries. The methods were developed for flame ionization detection (FID), mass spectrometric detection (MS). Further, headspace (HS) sampling for the investigation of solid samples like electrodes is reported. Limits of detection are reported for FID. Finally, the developed methods were applied to the electrolyte system of commercially available lithium ion batteries as well as on in-house assembled cells.

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1. Introduction

Today, lithium ion batteries (LIBs) are the only high energy density portable power sources commercially available. These devices have several advantages such as high energy and good cycling stability [1]. In general, LIBs consist of a lithium metal oxide cathode, a carbonaceous anode, a polyolefin-based separator and the electrolyte, which is mainly composed of a mixture of organic carbonates and a conducting salt [2]. The mixture of organic carbonates is composed of linear and cyclic carbonates such as dimethyl carbonate (DMC) and ethylene carbonate (EC). Besides the aging challenge of the LIBs, the flammable organic carbonates constitute a safety problem and limit the operative temperature of the batteries [3]. Therefore, quality control of the electrolyte is essential in this field of research. However, this task presents a main difficulty associated with the electrolyte being trapped into the electrodes and separator pores thus not readily available for analysis by conventional GC measurements.

The number of reported investigations on organic carbonates or carbonate-based electrolytes by gas chromatography (GC) is very limited in literature [4–6]. One of the first reports in this field was made by Kumai et al. at the end of the 1990s. They investigated the gas generation as a function of the cell potential [4]. The study of Mogi et al. addressed the decomposition of the conductive salt dissolved in PC on a nickel electrode [5]. Recently, a gas chromatography mass spectrometry (GC–MS) study was reported by Laruelle and co-workers [6]. In this latter work, the analyses of the aged carbonate-based electrolytes as well as the investigations on

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the electrolyte components after heating were performed. Further, Pelet et al. accomplished a separation method for ethylene carbonate (EC) and glycerol carbonate by GC–FID [7]. However, to the best of our knowledge, headspace methods for the direct analysis of other electrolyte components are, so far, not reported in the literature.

The focus of this work was to develop a GC method for both FID and MS detection to investigate pure organic carbonate solvents as well as carbonate-based electrolytes. In addition, a headspace-GC–MS method was developed to investigate the electrolyte wetting the surfaces of other cell components, such as the separator.

2. Experimental

2.1. Chemicals

Diethyl carbonate (DEC), dimethyl carbonate (DMC), ethyl-methyl carbonate (EMC) propylene carbonate (PC), ethylene carbonate (EC) and vinylene carbonate (VC) were used as received from UBE (Yamaguchi, Japan). The carbonates were diluted with either dichloromethane (DCM) or methanol, purchased from Sigma–Aldrich Chemie GmbH (Steinheim, Germany). All chemicals were of the highest quality available. Furthermore, electrolytes from aged, commercial and laboratory cells were analyzed.

2.2. Instrumentation

In this work, a Clarus® 600 gas chromatograph was used. With its built-in flame ionization detector and the hyphenation to a Clarus® 600C Mass Spectrometer both techniques, GC–FID and GC–MS were carried out. A further feature was coupled by transfer line to the above-mentioned GC–MS system – the Turbomatrix 40 Trap headspace sampler (firmware version 2.14.83) – to perform headspace GC–MS analyses. The instruments were controlled by the TurboMass 5.4.2 GC/MS software. All instrumental components were obtained from Perkin Elmer (Rodgau, Germany).

For the identification of compounds and to assign corresponding structural formulas, the National Institutes of Standards library (version 2.0) was used.

Chromatographic separation was performed on a Stabilwax® column (30 m × 0.32 mm × 0.25 μm) from Restek Corporation (Bellefonte, PA, USA).

2.3. GC–FID conditions

For all GC–FID analyses, helium was used as GC carrier gas, whose flow was maintained at a constant value of 1.2 mL min^{-1}. The injection volume of 1 μL was transferred to the injector maintained at 230 °C. The injector temperature was ramped from 30 °C to 230 °C as follows: The initial temperature (30 °C) was held for 3 min prior to increase up to 50 °C with a rate of 30 K min^{-1}. After holding this temperature for 5 min, the temperature was increased up to 230 °C (30 K min^{-1}) and hold for 8 min. The total duration of the GC analysis was 22.5 min.

2.4. GC–MS conditions

Also for all GC–MS analyses helium was used as the GC carrier gas, whose flow was maintained at a constant value of 1.2 ml L^{-1}. The injection volume of 1 μL was transferred to the injector maintained at 230 °C. The temperature gradient was ramped from 35 °C to 230 °C as follows: after holding the initial temperature for 3 min the temperature was increased with a rate of 30 K min^{-1} up to 50 °C and hold for 5 min; subsequently the temperature was increased up to 230 °C with the same temperature rate and then

held for 6 min. The total duration of the GC–MS analysis was 20.5 min. The transfer line was hold at a constant temperature of 150 °C. The mass spectrometer was operated in the positive electron ionization (EI) mode, the electron energy was 70 eV and the filament current was 250 μA. The mass range was 20 amu–200 amu for 20.5 min with solvent delays from 2.4 to 3.65 min and 14.76 to 15.15 min.

2.5. Headspace-GC–MS conditions

The helium gas flow was controlled via pressure and set to 21 psi. The headspace unit was thermostated at 60 °C. After equilibration of the sample for 1 min, the sampling was carried out. To avoid condensation inside the needle its temperature was set to 70 °C. The gaseous injection volume was transferred to the injector via a heated transfer line (120 °C). The GC temperature gradient was ramped from 35 °C to 230 °C as follows: the initial temperature of 35 °C was hold for 5 min; with a rate of 30 K min^{-1} the temperature was increased up to 50 °C and hold for 3 min; next, the temperature rate was set to 30 K min^{-1} to increase the column oven temperature up to 230 °C. This temperature was hold for 10 min. The total duration of the GC analysis was 54.0 min. The mass spectrometer was operated in the positive electron ionization (EI) mode, the electron energy was 70 eV and the filament current was 250 μA. The mass range was 25 amu–400 amu without solvent delays.

2.6. Sample preparation

For the determination of the limit of detection (LOD) by GC–FID, the organic carbonates (EC, DMC, EMC, DEC, VC and PC) were diluted with methanol. Five samples for each carbonate in a concentration range between 100 ppb and 100 ppm were analyzed.

For the development of a separation method for organic carbonates on a polar column, the samples were diluted with DCM to an end concentration of 1 mmol L^{-1}. For the determination of the detection limit, the samples were diluted with DCM.

Another approach was the electrolyte analysis of a commercially available, aged lithium-ion battery (LIB) from A123. Therefore, the aged LIB was fully discharged and then disassembled. The electrodes were separated and subsequently rinsed with PC. The rinsing solutions were analyzed without further treatments by GC–MS.

For headspace-GC–MS analyses the commercially available LIB was aged for about 1400 cycles with a charge and discharge rate of 1C between the voltage cut-off limits of 2.4 V and 3.6 V, at room temperature. Afterward the cell was discharged to 2.4 V for 3 h, and disassembled. The separator was transferred directly into a headspace vial.

3. Results and discussion

3.1. GC–FID method

Determining the limit of detection for the most common organic carbonates used in lithium ion batteries was carried out first. For each carbonate five samples in a concentration range between 100 ppb and 100 ppm were analyzed. As lower limit of detection, a signal to noise ration of 3 was accepted. The identified limits of detection are reported in Table 1.

A mixture of five carbonates (DMC, DEC, EMC, EC and PC) was analyzed by GC–FID. In Fig. 1 the resulting chromatogram is shown. The remarkable signal at the retention time $t_R = 8.5$ min is easily assigned to the solvent dichloromethane. DMC was detected at $t_R = 10.19$ min, EMC at $t_R = 11.32$ min, DEC at $t_R = 12.25$ min, PC at

Table 1
Limit of detection (LOD) for the common organic carbonates used in lithium ion battery electrolytes.

Analyte	DMC	EMC	DEC	VC	PC	EC
LOD	2 ppm	1 ppm	500 ppb	500 ppb	500 ppb	500 ppb

$t_R = 19.45$ min and EC at $t_R = 20.65$ min. The assignment was made via commercially available standards. These results indicate that the carbonates are baseline separated.

Further, two different carbonate-based electrolytes were analyzed. In Fig. 2, the GC−FID chromatogram of the mixture of EC/DEC (3:7, v/v) electrolyte is shown. Two signals were detected, besides the first peak with a retention time at $t_R = 8.5$ min, which is due to dichloromethane. By means of retention times, these two peaks were identified as DEC at $t_R = 11.8$ min and EC at $t_R = 19.2$ min.

Fig. 3 shows the GC−FID chromatograms of the mixture of EC/EMC (1:1, v/v) electrolyte. Three baseline-separated peaks were obtained in Fig. 3. The first peak at $t_R = 8$ min belongs to dichloromethane. By comparison of retentions times the peak at $t_R = 10.9$ min and $t_R = 19.2$ min can be assigned to EMC and EC, respectively.

3.2. GC−MS method

The electrolyte extracted from a commercially available LIB aged for 1400 cycles at room temperature was examined by GC−MS. The cell was cycled at a constant current of 1C in a voltage window of 2.4 V−3.6 V and had an initial capacity of 2.16 Ah and a final capacity of 2.06 Ah. No end of life criteria or intermediate check-ups was used. PC was used as electrode rinsing solvent to extract the electrolyte components. In Fig. 4 it is shown the total ion current (TIC) chromatogram of the GC−MS investigation of the anode rinsing solution, while that for the cation rinsing solution is presented in Fig. 5.

The chromatogram of the anode rinsing solution exhibits five main peaks, which were assigned to DMC, EMC, EC, 1,4-dioxane and [15]-crown-5-ether. The magnified area from 13.0 min to 14.25 min exhibits a number of peaks, which were identified as traces of vinylene carbonate (VC), 1,2-propanediol (from the washing process with PC), 1,2-ethanediol (which is a decomposition product of PC and EC), γ-butyrolactone (GBL) and *N*-methyl-2-pyrrolidinone
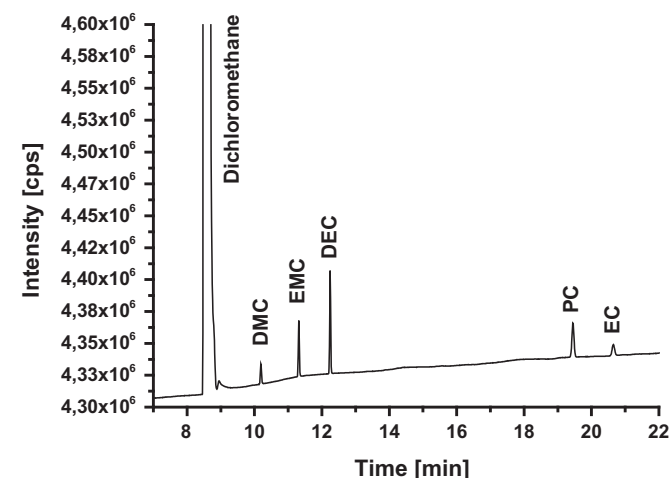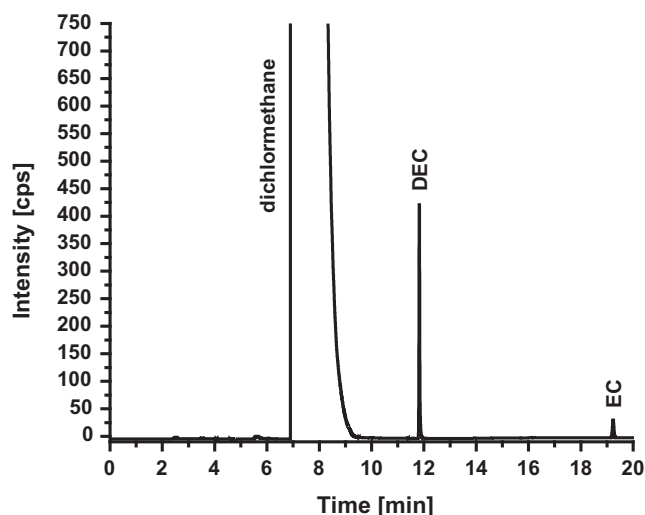

Fig. 2. GC−FID chromatogram of the carbonate-based electrolyte EC/DEC 3:7 containing 1 mol L^{-1} LiPF$_6$ diluted in dichloromethane.

(NMP). The assignment of the peaks was based on commercially available standards and resulting mass spectra. In Fig. 5, a lower number of peaks were detected. The main peaks were identified as DMC, EMC and EC. Also 1,4-dioxane, VC, NMP and caprolactam were identified.

Due to the respective peak areas, DMC, EMC and EC were identified as the main electrolyte components. However, the relative peak areas of DMC and EMC differ in the chromatograms of the electrode extracts. In contrast to the cathode electrolyte extract, the relative peak area of DMC is larger than that of EMC in the anode electrolyte extract. This evidence can be explained either by the higher decomposition of EMC at the anode or the more effective redox reaction of EC and DMC to EMC with corresponding alcohols at the cathode. Furthermore, VC and 1,4-dioxane were determined in the electrolyte extracted from the cathode. VC is a film forming additive, which supports the SEI formation at the anode by decomposing at potentials lower than 1.0 V. Monitoring a considerable VC peak in the cathode rinsing solution and a negligible VC peak at the anode confirmed the decomposition of VC at the anode.
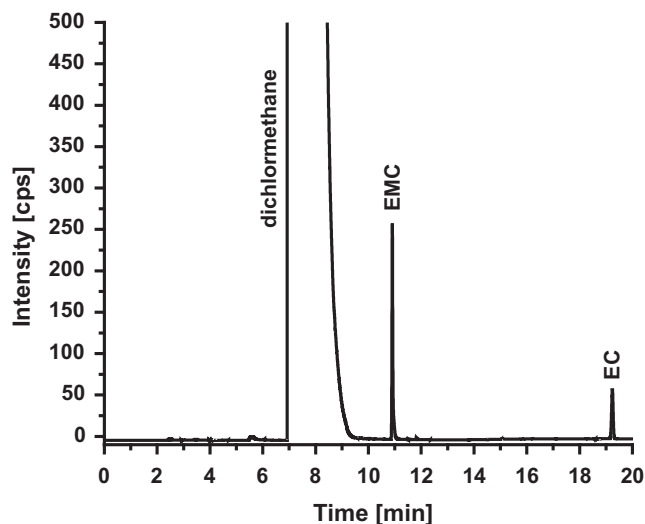

Fig. 1. GC−FID chromatogram of the analysis of five organic carbonates diluted in dichloromethane.

Fig. 3. GC−FID chromatogram of the carbonate-based electrolyte EC/EMC 1:1 containing 1 mol L^{-1} LiPF$_6$ diluted in dichloromethane.
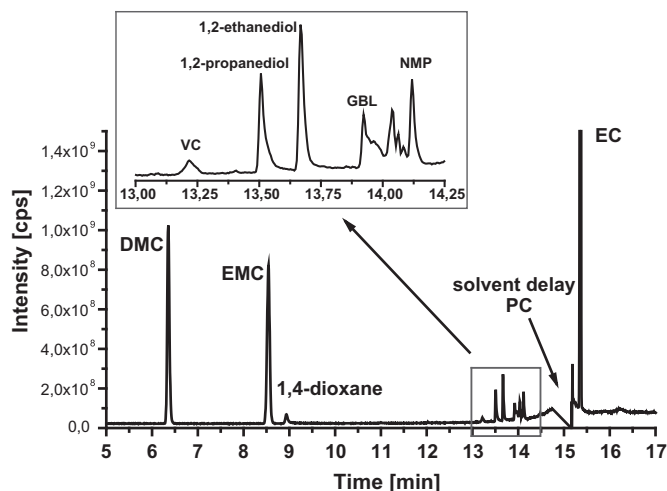
Fig. 4. TIC chromatogram of the GC–MS analysis of the anode wash solution.

Fig. 6. TIC chromatogram of the headspace-GC–MS analysis of the extracted separator.

Both observations lead to the conclusion that the electrolyte exchange through the separator is not very effective. Additionally, the unequal content of 1,4 dioxane in the two electrode extracts supports for its role as an additional film forming additive for the build-up of the anodic SEI.

Regarding the other compounds present in traces, *N*-methyl-2-pyrrolidinone (NMP) was identified in both electrolyte extracts. However, NMP is used as solvent for the electrode preparation and its presence as trace component is not unexpected. 1,2-propanediol and 1,2-ethanediol, present only in the anodic electrolyte extract, are originating from the decomposition of PC and EC, respectively. [15]-crown-5-ether and GBL, also present in the anodic electrolyte extract, are most likely formed by the complex decomposition reactions taking place at the anode during the SEI formation.

3.3. Headspace-GC–MS

The electrolyte-impregnated separator was extracted from a different commercial LIB aged for 1400 cycles at room temperature (25 °C) and transferred into a headspace vial. The cell was cycled at a constant current of 1C in a voltage window of 2.4 V–3.6 V and had an initial capacity of 2.16 Ah and a final capacity of 2.06 Ah. No end of life criteria or intermediate check-ups was used.
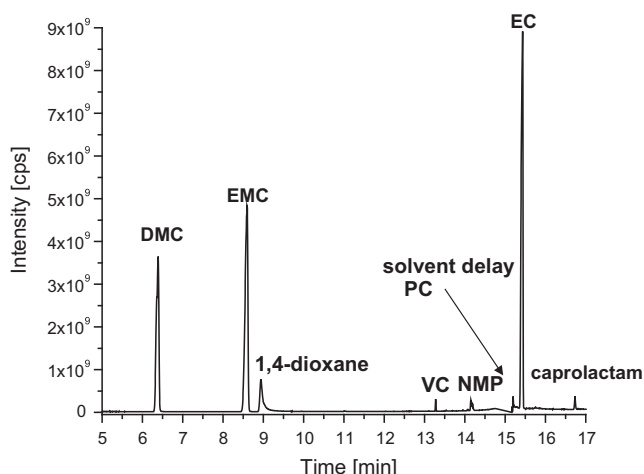
In Fig. 6, the total ion current (TIC) chromatogram of the headspace-GC–MS investigation of the separator is shown. The peaks in the chromatogram could be assigned to DMC, EMC, DEC, VC, EC and biphenyl based on commercially available standards and the mass spectra. DMC, EMC and DEC are identified, and VC, EC and biphenyl were also monitored. The reason of the small EC peak resulting from headspace-GC–MS investigation is clearly associated with the much lower volatility of this compound with respect to the linear carbonates (DEC, DMC and EMC). Furthermore, the peak area of every compound is depending on the response factor, which is obtained by analyzing a known quantity of the specific compound and calculation of the peak area. For quantitative analysis, the method parameters have to be further investigated and optimized.

4. Conclusions

In this work, a separation method for the five carbonates DMC, DEC, EMC, PC and EC was developed using GC–FID. Furthermore, analyses of carbonate-based electrolytes were carried out. Transferring this method to GC–MS, the electrolyte of an aged, commercial lithium-ion cell was analyzed. Three main components (EC, EMC and DMC) were identified in the electrolyte. Furthermore, the film-forming additive VC was determined. Due to the different relative peak areas in the anode and cathode rinsed electrolytes, a very limited electrolyte mixing through the cell separator is assumed even upon a relatively long cell aging time (ca. 4000 h). A different content of 1,4-dioxane was identified in the rinsed electrolytes from the two electrodes, thus indicating that this compound might be used as a film-forming additive for the SEI build-up as well. The detection of NMP in both electrolyte extracts implies that this substance was used as solvent for the electrode procedure. In general, NMP should be removed out of the electrodes before the battery is built.

Furthermore, the developed GC–MS method was modified and applied to a headspace-GC–MS setup and separator samples could be analyzed successfully. Biphenyl, a common additive in LIBs, was found besides the carbonates. However, a further improvement of the headspace-GC–MS setup and procedure are necessary to obtain quantitative information about the electrolyte composition.

In conclusion the developed methods were able to separate the organic carbonates and furthermore, some common used additives and solvent compounds, which are used during the preparation of lithium ion batteries.

Fig. 5. TIC chromatogram of the GC–MS analysis of the cathode wash solution.

Acknowledgments

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